

EXHIBIT "1"

SERIAL NO.: 10/041,111

DOCKET: TUC920000094US1

ELECTRICALLY & THERMALLY CONDUCTIVE MATERIALS

Technical Bulletin A8

Aremco offers a broad line of electrically and thermally conductive materials which provide solutions to a variety of electrical, electronic and thermal design problems throughout industry...

PRODUCT HIGHLIGHTS

Aremco-Bond™ 525

- Electrically Conductive, Silver-Filled, One-Part Epoxy Paste.
- Good Chemical Resistance and Mechanical Strength to 340 °F.

Aremco-Bond™ 556

- Electrically Conductive, Silver-Filled, 1:1 Epoxy Paste.
- Good Corrosion Resistance and Mechanical Strength to 340 °F.

Aremco-Bond™ 568

- Thermally Conductive, Aluminum-Filled, 1:1 Epoxy Paste.
- Excellent Mechanical Strength to 400 °F.

Aremco-Bond™ 805

- Thermally Conductive, Aluminum-Filled, Two-Part Epoxy Paste.
- Low Shrink Rate & Excellent Mechanical Strength to 570 °F.

Aremco-Bond™ 860

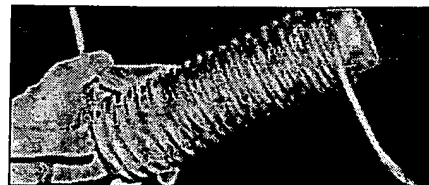
- Thermally Conductive, Aluminum Nitride Filled, 1:1 Epoxy Paste.
- Exceptional Mechanical and Thermal Properties to 400 °F.

Pyro-Duct™ 597

- Electrically and Thermally Conductive, Silver-Filled, One-Part System.
- Inorganic System for Adhesive & Coating Applications to 1200 °F.

Pyro-Duct™ 598

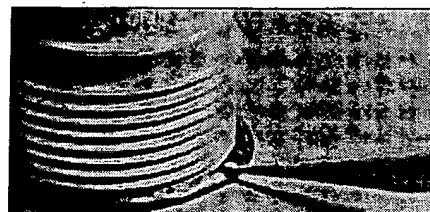
- Electrically and Thermally Conductive, Nickel-Filled, One-Part System.
- Low Viscosity, Inorganic Coating for Applications to 1000 °F.



Aremco-Bond™ 568 bonds copper heat exchange tube to steel core.



Pyro-Duct™ 598-C metallizes handbag accessory for plating.



Aremco-Bond™ 805 bonds aluminum heat sink to a power semiconductor device.

PROPERTIES		ELECTRICALLY AND THERMALLY CONDUCTIVE				THERMALLY CONDUCTIVE		
Product Number		525	556	597A/C ^①	598A/C ^①	568 ^②	805	860 ^②
Handling & Curing	Filler	Silver	Silver	Silver	Nickel	Aluminum	Aluminum	Aluminum Nitride
	Mix Ratio by Weight, resin:hardener	NA	1:1	NA	NA	1:1	100:12	1:1
	Mixed Specific Gravity, gms/cc @ 25 °C	1.85	2.8	2.3/2.1	2.87/1.5	.85	1.66	1.9
	Mixed Viscosity, @ 25 °C, cps	Paste	Paste	Paste/Paste	22,000/480	Paste	11,000	Paste
	Pot Life, 100 gm mass @ 25 °C, hrs	N/A	1	N/A	N/A	4.0	≤ 1.0	4.0
	Recommended Cure, hr/°F	2/300	24/RT	2/RT + 2/200	2/RT + 2/200	2/200	2/100 + 2/200	2/200
Cured Properties	Alternate Cure, hr/°F	6/250	4/170 or 2/210	—	—	24-48/RT	24-48/RT	24-48/RT
	Temperature Resistance, °F (°C)	340 (171)	340 (171)	1200 (649)	1000 (538)	400 (204)	572 (300)	400 (204)
	CTE, in/in/°F x 10 ⁻⁶ (°C)	29.0 (52.2)	13.9 (25.0)	9.6 (17.3)	6.5 (11.7)	33.0 (60.0)	25.0 (45.0)	18.7 (33.3)
	Thermal Conductivity, Btu-in/hr-ft ² -°F	62.2	65.0	63.1	17.9	9.0	12.5	8.5
	Tensile Shear Strength, psi ^③	2,500	1,500	—	—	1,400	1,200	1,375
	Volume Resistivity, ohms-cm	0.01	0.0052	0.0002	0.005	1.0 x 10 ⁵	1.0 x 10 ⁵	1.0 x 10 ¹⁵
	Dielectric Strength, volts/mil	—	—	—	—	80	50	250
	Chemical Resistance	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Excellent
	Color	Silver	Silver	Silver	Dark Gray	Gray	Gray	Gray
	Reference Notes	Application Notes						
	① Order 59x-A for adhesive uses; 59x-C for coating uses.	Surface Preparation: All surfaces must be free of oil, grease, dirt, corrosives, oxides, paint or other foreign matter. Sand blast or abrade non-porous surfaces, or etch using Aremco's Corr-Prep™ CPR2000.						
	② Available as fast-set or low viscosity systems. Add "LV" for low viscosity (eg. 568-LV), "FS" for fast-set (eg. 568-FS).	Mixing: Two-component products should be mixed thoroughly to a uniform consistency. Preheat high viscosity epoxies to approximately 125 °F to facilitate pouring and mixing. Use Aremco's 9700 or 9800 50 ml dispensing systems for precise mixing of two-component products.						
	③ Tested according to ASTM D1002-94. This is a standard test method for determining the shear strength of single lap-joint metal coupons in tension loading.	Application: In most cases, the adhesive should be applied to both surfaces maintaining a glue line of less than 10 mils. After assembling the parts, pressure should be applied to the assembly to prevent warpage and reduce air entrapment. Refer to curing guidelines in above property chart.						

AREMCO PRODUCTS, INC.

P.O. Box 517, 707-B Executive Boulevard, Valley Cottage, NY 10989

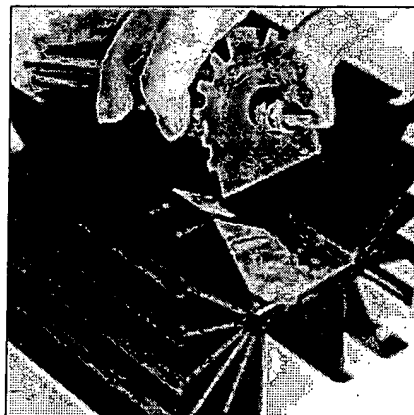
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HEAT-AWAY™ GREASES

Aremco's Heat-Away™ thermal greases are ceramic and metal-filled silicone systems which offer exceptional thermal and electrical properties to 550 °F. These materials are used in high-power electronic devices, heat pipes, and other heat exchange systems.

PROPERTIES	THERMALLY CONDUCTIVE GREASES				
Product	637	638	639	640	641
Filler	Alumina	Aluminum Nitride	Aluminum	Copper	Silver
Temperature Limit, °F	-60 to +550	-60 to +550	-60 to +550	-60 to +550	-60 to +550
Thermal Conductivity, W/m-°K	0.475	2.23	3.04	4.68	5.58
Dielectric Strength, volts/mil	300	300	40*	4*	Conductive
Volume Resistivity @ RT, ohm-cm	10 ¹⁴	10 ¹⁴	10 ⁴	10 ³	NA
Chemical Resistance	Excellent	Excellent	Excellent	Excellent	Excellent
Water Absorption	Nil	Nil	Nil	Nil	Nil
Solids, %	100	100	100	100	100
Specific Gravity, gms/cc	2.42	2.27	1.35	1.33	1.40
Color	White	Gray	Aluminum	Copper	Silver

*Caution: Exposure to voltages in excess of rated maximum can cause permanent electrical leak paths.



Heat-Away™ 638 used as a heat transfer grease between a high temperature ballast resistor and an aluminum heat sink.

Refer to Price List for complete order information.

Aremco Products makes no warranty express or implied concerning the use of this product.

The user assumes all risk of use or handling whether or not in accordance with directions or suggestions, or used singly or in combination with other products.

EXHIBIT “2”

SERIAL NO.: 10/041,111

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Silicon, Si

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Subcategory: Metal; Nonferrous Metal; Pure Metallic Element; Semiconductor

Component Wt. %

Si 100

Material Notes:

Information provided by Silicon Casting, Inc. and the references.

No vendors are listed for this material. Please [click here](#) if you are a supplier and would like information on how to listing to this material.

Physical Properties

	Metric	English
Density	2.329 g/cc	0.0841 lb/in ³
a Lattice Constant	5.43072 Å	5.43072 Å
Volume Compressibility, 10 ⁻¹⁰ m ² /N	0.306	0.306

Mechanical Properties

Knoop Microhardness	11270	11270	N/mm ² I
Modulus of Elasticity	112.4 GPa	16300 ksi	
Compressive Yield Strength	120 MPa	17400 psi	
Bulk Modulus	98.74 GPa	14300 ksi	
Poisson's Ratio	0.28	0.28	
Shear Modulus	49 GPa	7110 ksi	

Electrical Properties

Electrical Resistivity	0.01 ohm-cm	0.01 ohm-cm	
Magnetic Susceptibility	-3.9e-006	-3.9e-006	
Critical Superconducting Temperature	6.7 - 7.1 K	6.7 - 7.1 K	6.7-7.1 K from 12.0-13.0
Dielectric Constant	11.8	11.8	
Band Gap	1.107 eV	1.107 eV	

Electron Mobility, cm ² /V-s	1900	1900
Hole Mobility, cm ² /V-s	500	500

Thermal Properties

Heat of Fusion	<u>1800 J/g</u>	774 BTU/lb
CTE, linear 20°C	<u>2.49 µm/m-°C</u>	1.38 µin/in-°F
CTE, linear 250°C	<u>3.61 µm/m-°C</u>	2.01 µin/in-°F
CTE, linear 500°C	<u>4.15 µm/m-°C</u>	2.31 µin/in-°F
CTE, linear 1000°C	<u>4.44 µm/m-°C</u>	2.47 µin/in-°F
Heat Capacity	<u>0.702 J/g-°C</u>	0.168 BTU/lb-°F
Thermal Conductivity	<u>124 W/m-K</u>	861 BTU-in/hr-ft ² -°F
Melting Point	<u>1412 °C</u>	2570 °F
Heat of Formation	324 kJ/mol	324 kJ/mol
Debye Temperature	<u>372 °C</u>	702 °F

Optical Properties

Refractive Index	3.49	3.49
Reflection Coefficient, Visible (0-1)	0.3 - 0.7	0.3 - 0.7
		varies irregularly with wavelength

Descriptive Properties

Crystal Structure	Cubic	Diamond Structure - Space Group Fm-3m
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**References** for this datasheet.

Some of the values displayed above may have been converted from their original units and/or rounded in order to display the information in a consistent manner. If you require more precise data for scientific or engineering calculations you can click on the property value to see the original value as well as raw conversions in the units. We advise that you only use the original value or one of its raw conversions in your calculations to minimize rounding error. We also ask that you read our disclaimer and terms of use regarding this information. [Click here](#) to view all the property values for this datasheet as they were originally entered into the database.

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EXHIBIT “3”

SERIAL NO.: 10/041,111

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Diffusion of Low Molecular Weight Siloxane from Bulk to Surface

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C. L. Mirley,¹ J. Ronzello and S. A. Boggs

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ABSTRACT

Silicone-based materials for outdoor insulators have the advantage that low molecular weight (LMW) components migrate through the material and coat the surface, thereby restoring hydrophobicity over a period of hours. By measuring the IR absorption of siloxane migrating to the silicone surface through a thin carbon coating, the time constant for migration was calculated. According to the time dependence of IR-absorbance, the time constant for migration ranged from 1.6 to 5.3 h depending on alumina trihydrate (ATH) filler concentration.

1 INTRODUCTION

SILICONES provide the advantages of hydrophobicity, resistance to chemical attack, and adequate electrical properties for many outdoor HV applications. The room temperature vulcanized (RTV) silicones are easily handled and applied as coatings. As a result, they have gained acceptance as a coating for porcelain insulators in order to improve performance under polluted conditions. The high temperature vulcanized (HTV) silicones have improved mechanical strength over RTV and are employed as material for insulator sheds, especially for transmission class suspension insulators, bushing sheds, etc. Silicone HV sheds are gaining market share as a result of improved tolerance to pollution, ease of handling and installation, and resistance to vandalism.

In general, silicones have superior water repellency (hydrophobicity) to most organic polymeric insulation materials, such as ethylene propylene diene monomer (EPDM) and ethylene vinyl acetate (EVA). Improved hydrophobicity suppresses leakage current and partial discharge under heavily contaminated conditions [1-4]. Even if a silicone surface loses hydrophobicity as a result of severe weather or continuous exposure to the arcing, it can recover hydrophobicity over time under dry conditions as a result migration of LMW siloxanes from the bulk to the surface, where they tend to coat even the pollution on the shed surface, providing a hydrophobic surface under heavily polluted conditions [2, 3]. The recovery of hydrophobicity provides reduced leakage current and recovery of the superior insulating properties of the surface under wet and polluted conditions. Thus the migration of LMW siloxanes improves the long term stability of silicones under polluted conditions. These outstanding insulation properties of silicones are the result of their unique chemical structure. Silicone based insulators and coatings are manufactured primarily from polydimethylsiloxane (PDMS) structured with siloxane bonds (Si-O) as the backbone and methyl groups (-CH₃) as the functional substituents. The methyl group has the lowest critical surface tension among common organic substituents, except for the fluoromethylene group (-CF₂). Thus silicones have hydrophobicity comparable to that of some fluoride polymers, such as polytetrafluoroethylene

(PTFE). Silicones normally contain a broad molecular weight distribution of siloxane components, from silicone fluid (oil-like with molecular weight <25000) and silicone polymer which has various backbone chain lengths. The smaller LMW components can move easily through the bulk polymer with the result that they distribute fairly uniformly in the bulk and concentrate at the surface to minimize the surface free energy. The mobility of LMW components is fundamental to the recovery of hydrophobicity of the silicone surface after hydrophobicity has been reduced through heavy weathering (e.g., washing away of the LMW components by rain) or heavy pollution. Thus evaluation of mobility of the LMW components and recovery of LMW components on the insulator surface is fundamental to understanding the long term reliability of silicone HV apparatus.

The recovery of hydrophobicity of silicones has been discussed based on both field and laboratory experience [2-10]. Measurement of contact angle between a water droplet and the polymer surface has been employed to determine the water repellency of polymeric materials. A number of investigators have attempted to determine the diffusion of LMW siloxanes in RTV materials using this technique [3, 5-10].

Using energy dispersive X-ray (EDX) analysis and X-ray mapping (XRM) of a silicone rubber surface covered with 2 μ m thick graphite paste, the X-ray intensity attributed to siloxanes was observed to increase over time, indicating the migration of the LMW to the surface [6]. However, this approach suffers from having to make the measurement in vacuum where the lowest molecular weight components are likely to volatilize and be lost to the analysis.

Optical analysis using FTIR spectroscopy has been attempted under atmospheric condition to quantify the migrated components directly [7]. By measuring the IR-absorption from silicone residue transferred from the bulk surface onto an attenuated total reflection (ATR) optical element, KRS5 crystal, the migration of LMW components was established through increased absorbance vs. time [7, 9]. From such measurements, various investigators have estimated time constants for recovery of hydrophobicity ranging from ~20 to ~200 h. The present contribution

employs ATR FTIR spectroscopy to measure the migration of LMW silicones through an evaporated carbon coating which acts as a proxy for the insulator surface contamination. Infrared absorption from spectral features characteristic of LMW siloxanes was monitored continuously during the experiments. The time constant to steady state was calculated also for several silicone materials which had various concentrations of inorganic filler added. The measurements were made under atmospheric conditions in contrast to other recent measurements which were made in vacuum.

2 EXPERIMENTS

2.1 FTIR MEASUREMENTS OF CARBON-COATED SURFACE

As noted above, migration of LMW silicones from the bulk through a carbon coating were measured using ATR FTIR spectroscopy in this work. FTIR is a common technique to investigate chemical structures of polymers, and the ATR method is employed to evaluate the material surface. In this work, a thin carbon layer was deposited on the RTV silicone samples and the carbon-coated surface was subjected to the ATR FTIR measurements. Prior to carbon coating, the surface of the silicone samples was wiped with ethanol to remove LMW siloxanes. A 50 to 70 nm coating of carbon was evaporated onto the sample in vacuum. Although exact control of the carbon layer is difficult, the conditions of the evaporation were fixed in terms of vacuum level, evaporating time, distance between sample and carbon electrodes, etc. Sample coating was completed within ~5 min, and the sample was never exposed to vacuum more than 30 min. Such coating probably has a very large surface area and represents a worst case in terms of pollution. However, the primary purpose of the carbon was to form a 'solid' barrier or surface through which the FTIR cannot record. We could not employ a porous coating as a substitute for contaminants, or presumably the FTIR would see through it. It has already been suggested that such a carbon layer is suitable for the observation of LMW migration to the surface as the substitute of contaminants on field exposed insulators [6].

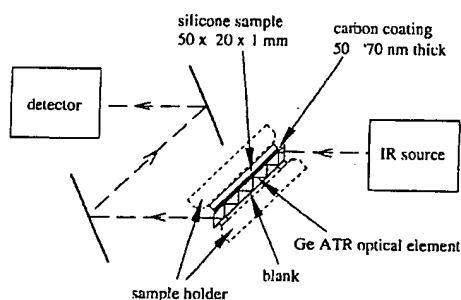


Figure 1. Optical system of ATR FTIR measurement.

The carbon coated surface contacted one side of the germanium total internal reflection element. The other side of the element faced a blank to prevent needless attenuation of the IR source. The angle of incidence for the IR source was 45° (Figure 1). As the pressure applied by the sample holder had an effect on the rate of siloxane migration, this pressure was controlled through careful torquing of the test jig. Samples of RTV

were examined as a function of the alumina trihydrate (ATH) filler concentration. Samples for the filled RTV were cast on a smooth substrate in the form of 50×20×1 mm thick films. The IR absorption spectrum was measured soon after application of the carbon coating and periodically over the next 12 h.

For the investigation of LMW siloxane migration, the influence of the ambient temperature has been discussed [6]. Therefore, the sample and the reflection element were kept under constant conditions at room temperature during the measurements. The ambient temperature was constant at 20°C.

2.2 GC-MS MEASUREMENT OF MOBILE LMW SILOXANE

After the FTIR measurements, a small amount of oil-like residue was found on the surface of the Ge ATR optical element. This residue was analyzed using a gas chromatography (GC) mass spectrometer (MS) fitted with a direct dynamic head space accessory in the heated injection port of the GC [11]. The GC-MS measurement is employed for evaluation of the molecular weight distribution and chemical identification of polymeric materials.

The residue was wiped off the Ge ATR element using glass wool. The glass wool was placed in a glass tube that was heated to 200°C for 2 min. Volatile components, released by heating, were injected into a methyl silicone capillary GC column which was heated from 35 to 300°C, at 15°C/min [12]. The output from the GC column was passed to a mass selective detector for chemical identification and quantification of the volatile components. The MS has a range of 10 to 1000 atomic mass units.

2.3 SAMPLE PREPARATION

Silicone samples were prepared with 0, 20, 40, and 60%wt ATH concentration in order to investigate the relationship between ATH filler concentration and rate of siloxane migration. The average diameter of the ATH filler was 13 μ m. The RTV silicone matrix and treated ATH filler were mixed with trifluoro-trichloroethane (CF_3CCl_3) solvent and cast into 1 mm thick sheet samples on an acrylic plate. Samples were left at room temperature for at least a day to allow the solvent to evaporate. The surface adjacent to the substrate was used for the ATR spectroscopic analysis. This RTV was a commercial grade from a material supplier and is used for the manufacture of silicone rubber coatings applied to station post insulators. This material was defined as one-part solventless silicone rubber, without corrosive byproducts and had a cure time of 24 to 72 h. After exposure at room temperature for >24 h, the residual solvent concentration should be very small because the solvent vapor can easily evaporate through the silicone rubber [13].

Photographs taken using a scanning electron microscopy (SEM) of the cross section of RTV silicone samples with 0, 20, 40, and 60%wt ATH are shown in Figure 2(a) to (d). The SEM micrographs indicate that the fillers were well dispersed in the RTV silicone matrix. The micrographs also indicate good adhesion of the RTV to the silane-treated ATH particles. Figure 3 shows the surface of RTV sample with 60%wt of ATH as employed for the FTIR measurement. The surface is extremely smooth with little exposed ATH in spite of the high filling concentration. The surface roughness of the measured samples did not depend on filler concentrations.

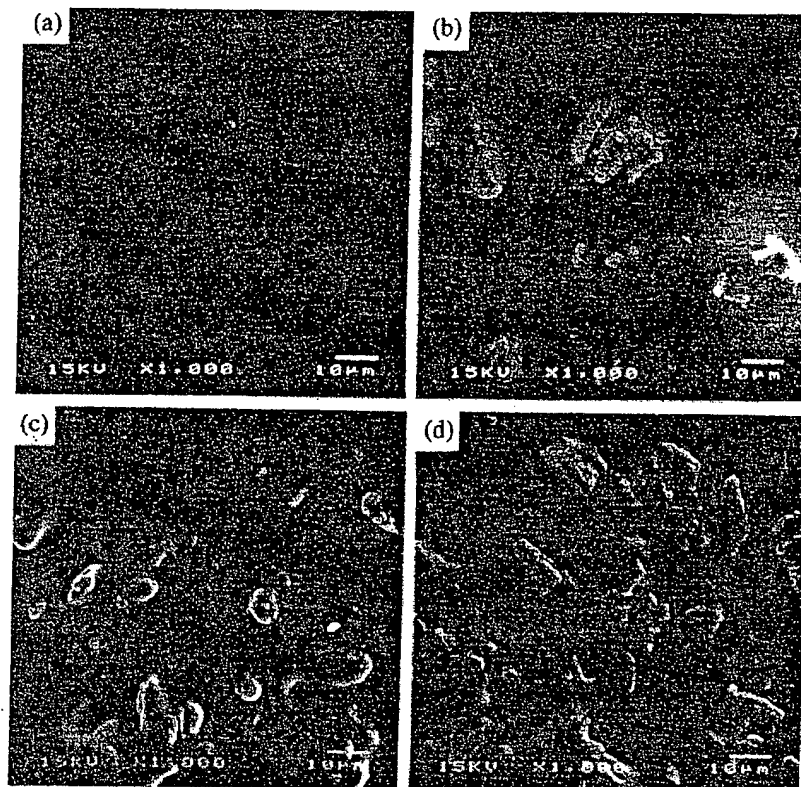


Figure 2. SEM photographs of the cross section of RTV silicone samples with various ATH filler concentrations. (a) 0%wt, (b) 20%wt, (c) 40%wt, (d) 60%wt ATH.

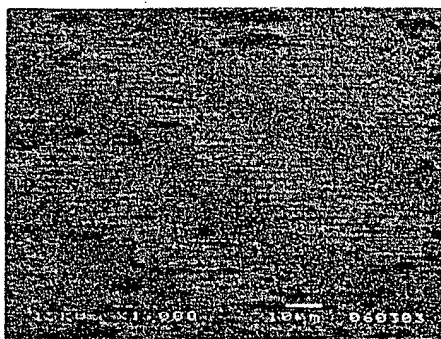


Figure 3. SEM photograph of the surface of RTV sample with 60%wt ATH filler.

The surface of the samples was smooth and provided good contact with the ATR. A larger concentration of polymer matrix in the surface region is normal in spite of the filler concentrations of up to 60%wt. However, the high surface concentration of PDMS probably does not play an important role in LMW migration to the surface from the bulk, as the filler size is about 10 μm and the larger concentration of PDMS must be limited to a very thin layer of a few microns near the surface which is small compared to the 1 mm thick samples which is typical of field-installed coatings [14].

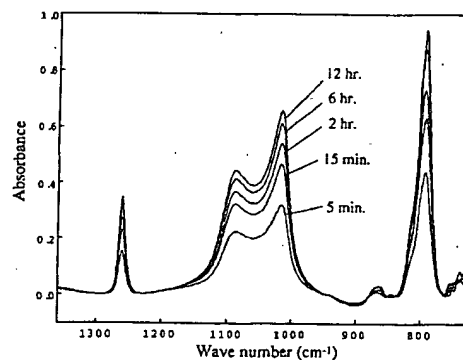


Figure 4. ATR FTIR absorption spectra of a carbon coated silicone sample with 60%wt ATH filler as a function of time after the carbon coating was applied.

3 RESULTS AND DISCUSSION

3.1 IR-ABSORPTION OF LMW SILOXANE

Figure 4 shows ATR FTIR absorption spectra as a function of time after the carbon coating was applied to the surface of an RTV silicone sample with 60%wt of ATH filler. The absorbance peaks at 1260, 1015, and 795 cm^{-1} correspond to the molecular vibrations for the $-\text{CH}_3$ symmetric

bend, the Si-O-Si symmetric stretch, and the Si-C symmetric stretch, respectively [15]. The magnitude of the absorbance of these three bands as a function of time is plotted in Figure 5. As can be seen from this Figure, the absorbance, which is proportional to the concentration according to Beer's law, of these species increases with time and reaches an asymptotic value after 12 h.

The ATR FTIR technique suffers from a number of disadvantages that limits its usefulness for quantitative analysis of polymer materials. Often, ATR FTIR data are normalized by defining a reference peak of IR spectra and then by comparing the observed changes to the intensity of the reference peak. However, these problems with the application of the ATR FTIR technique for the quantitative analysis arise due to difficulties in ensuring consistent contact between the polymer material and the ATR. In this work, we obtained the IR spectra for a sample in a static condition, with no change of contact between the ATR crystal and the sample. Therefore, we could compare the peak height, which were calculated from base lines, directly for a sample. The purpose of the present measurements was to compare the time constant of LMW diffusion of the samples with various filler concentrations, not to know the absolute spectral magnitude.

With regard to the sample roughness, the polymer normally forms a smooth skin over the filler as mentioned above. If the polymer matrix is lost, the roughness changes [2]. But we were not weathering our samples, so the surfaces were all in virgin condition with the skin in contact. Thus one would expect very smooth surfaces with little variation in surface roughness and the good contact between the surface and the ATR could be kept during the measurement.

3.2 CALCULATION OF THE TIME CONSTANT FOR MIGRATION

The time constant for migration of the LMW siloxanes was computed by fitting the following equation to the measured data,

$$A = K(1 - \exp[-a(t + B)]) \quad (1)$$

where A is the absorbance as function of time, K is the absorbance at saturation, a is a constant which has a dimension of inverse time, t is the elapsed time, and B is the time offset. $t = 0$ was defined as the time at which the carbon coating was completed.

Theoretical investigations published related to adsorption data for a penetrant solute indicate that the diffusivity of the solute is related to molecular weight, where the equation defining the boundary conditions was given by Ficks second law [16-17]. The constant $1/a$ was represented as a relaxation time of penetrant concentration of solute (silicone liquid) [18]. The fitted curves and calculated values of K , a , B for each absorbance peak are also shown in Figure 5. The time constant for each absorption peak, $1/a$, was about the same at 5.3 ± 0.7 h for the samples with 60%wt ATH.

We could estimate the diffusion coefficient if we made gross simplifications to the geometry and calculated the slope of the IR absorbance for the initial LMW diffusion. However, such a result would not be very meaningful compared to previously published data, where the diffusion of LMW siloxane in silicones or the other rubber materials has been described as a function of the square root of time, and the diffusion coefficient has been calculated [17-20]. The diffusion of LMW siloxane in

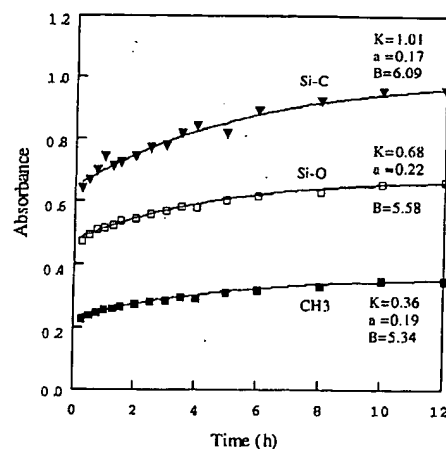


Figure 5. Time dependence of IR absorption of a carbon coated silicone sample with 60%wt ATH filler (symbols). Lines show the fitted curves which were calculated using Equation (1).

the present experiments is limited by the boundary condition at the surface, because the surface concentration approaches an equilibrium concentration. Although the time dependence of the IR-absorbance may be related to the square root of time at very short times, the approach to equilibrium is described better by an exponential function.

3.3 RELATION BETWEEN ATH CONCENTRATION AND TIME CONSTANT

The relationship between the ATH filler concentration and the time constant for siloxane migration is given in Figures 6(a) to (c), which show the time dependence of IR absorbance for samples with filler concentrations of 0, 20, and 40%wt ATH. Figure 7 summarizes the time constants as a function of filler concentration for the various absorption lines. The ATR absorbance measurements indicate that the time constant increases with increasing filler concentration.

Because the purpose of these measurements was to compare the time constant of LMW diffusion of the samples of various filler concentration, rather than to determine the absolute spectral magnitude, we normalized the IR absorbance to the saturated value K and offset time B . Figure 8 shows the approach to equilibrium for the various filler concentrations with K normalized to 1 and B normalized to 0.

Our data for the time constant are consistent with those of [9] and indicate, as might be expected, that the rate of migration decreases with increasing filler concentration, presumably for two reasons. First, the available PDMS polymer cross section available for diffusion decreases with increased filler concentration, and second, for high enough filler concentrations the percolation path for LMW migration will increase with increasing filler concentration. However, direct comparison of the time constants measured in the present work with those of [9] is difficult as a result of differing experimental conditions.

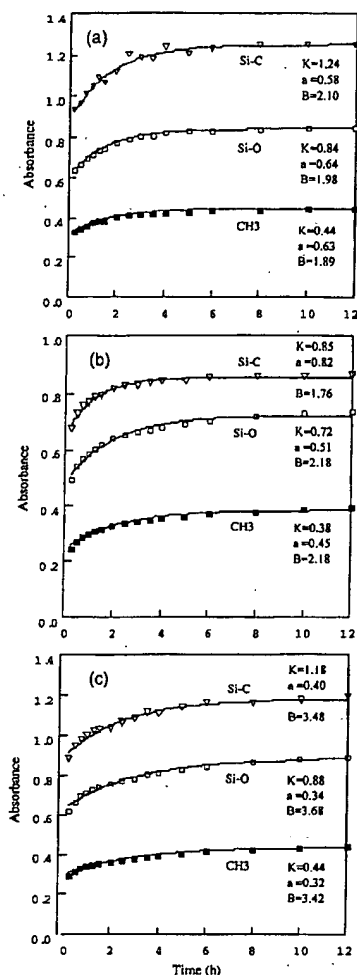


Figure 6. Time dependence of IR absorption of carbon coated silicone samples with various filler concentrations. (a) 0%wt, (b) 20%wt, (c) 40%wt ATH filler.

3.4 RECOVERY OF HYDROPHOBICITY OF CARBON-COATED SILICONE SURFACE

Advancing water contact angle was measured using a pendant drop apparatus equipped with a sessile contact angle cell. Water contact angle analysis has been used to monitor changes in the hydrophobicity of silicones as a function of time since larger water contact angles indicate a more hydrophobic surface [5, 8, 9]. The carbon coated RTV silicone samples were placed in the contact cell and a 10 μ l drop of distilled, de-ionized water was used as the probe solvent. The measurements were performed at a constant ambient temperature of 20°C. The datum reported for each contact angle is the average of five measurements.

Figure 9 shows the results of the contact angle measurement for the RTV silicone samples. Recovery of hydrophobicity was observed as increase of the contact angle with time for each samples. The surface of the

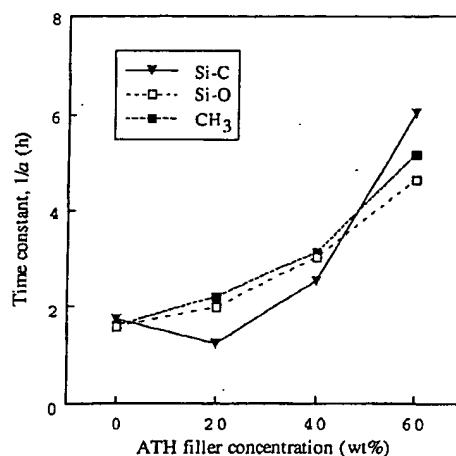


Figure 7. Relationship between ATH filler concentration and time constant of LMW siloxane migration.

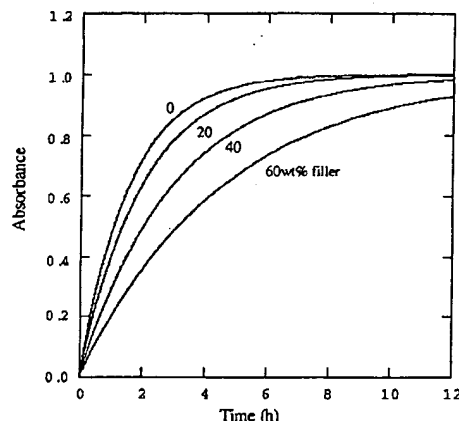


Figure 8. Approach to equilibrium of the LMW siloxane migration for various filler concentrations, with K normalized to 1, and B normalized to 0.

RTV samples showed good hydrophobicity before the carbon coating application, and the contact angle was constant at $\sim 113^\circ$ for all filler concentrations. However, the carbon coated surface had lower hydrophobicity ~ 4 h after the coating, and the contact angle increased with time. The recovery rate was influenced with the filler concentrations in a manner similar to the measured time dependence of the LMW migration observed in the IR absorbance.

3.5 MOLECULAR WEIGHT DISTRIBUTION OF MOBILE LMW SILOXANE

Figure 10 shows the GC spectrum of the oil-like material removed from the Ge ATR optical element after exposure to RTV sample. Several peaks were observed corresponding to the siloxane $[\text{Si}(\text{CH}_3)_2\text{O}]_n$ molecules, with $n = 6$ to $n = 15$ representing the number of siloxane units. The largest concentration was at $n = 12$ units (mass range 888 g/mol). This provides a good indication of the LMW siloxane species

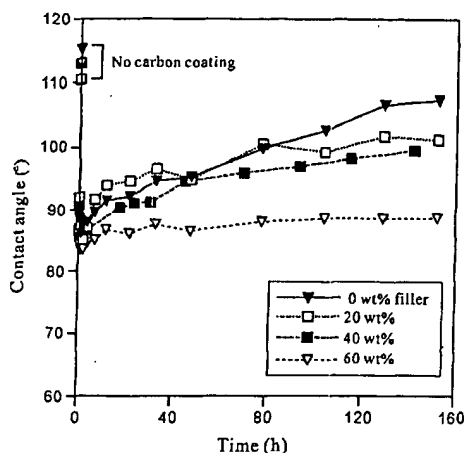


Figure 9. Time dependence of contact angle of carbon coated silicone samples with various filler concentrations.

which migrate to the surface to provide hydrophobicity. The data agrees with previous GC-MS measurements by the authors of the LMW siloxane species in virgin and field-aged samples of RTV [21].

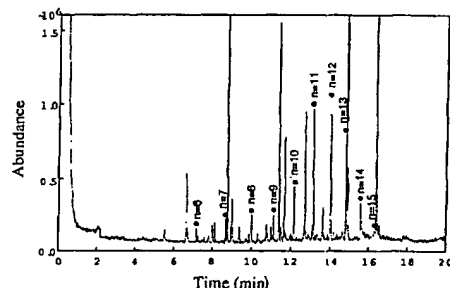


Figure 10. Gas Chromatograph of the oil-like residue on the Ge ATR optical element. Symbols (●) correspond to siloxane molecules.

4 CONCLUSIONS

By measuring the ATR FTIR absorption spectrum of siloxanes which migrate through a carbon coating on a silicone surface, the time constant for siloxane migration has been measured as a function of ATH concentration. The time constant was found to range from ~1.6 h at 0%wt filler concentration to ~5.3 h for 60%wt filler concentration. The measured time dependence of the LMW migration through a carbon coating is in good agreement with the measured recovery in hydrophobicity as determined by contact angle measurements. GC-MS measurements determined that the LMW siloxane species contained from 6 to 15 siloxane units with the maximum concentration at 12 siloxane units. These data should provide a good indication of the time required for recovery of hydrophobicity.

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Outgassing in Silicone Flexible Heaters

By Kareem M. Monib, Arlon Inc., Silicone Technologies Div.

Understanding the sources and mechanisms of outgassing has led to the development of low outgassing silicones.<

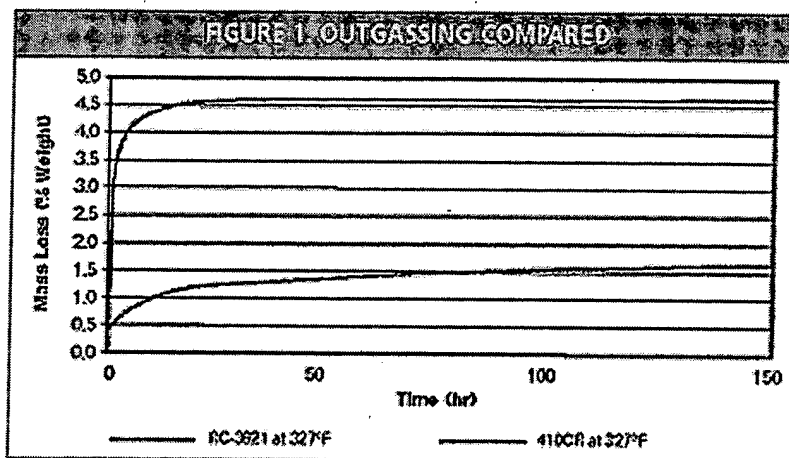


Figure 1. Comparison of total mass lost during the outgassing of two silicone materials.

Silicone is an outstanding material for flexible heaters because of its high temperature resilience and elastomeric mechanical properties. However, dealing with the outgassing of silicone is an area of concern, especially with sensitive applications. Even in areas where contamination is not a major issue, the presence of outgassing is an olfactory nuisance.

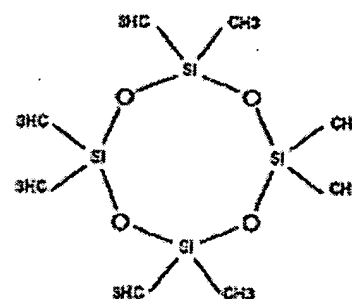
The aerospace, biomedical and semiconductor industries all use flexible silicone heaters where outgassing can be problematic. Recent progress has occurred in understanding and reducing silicone outgassing. Although outgassing appears to be a simple phenomenon, it occurs due to a number of factors. For example, outgassing depends on the amount and type of filler and catalyst used. Other factors, including the cure history of the silicone, degree of cross-linking, operating temperature, and whether the silicone is encapsulated or open to the atmosphere, also are important. In order to understand how to reduce outgassing, one first should examine the sources of outgassing and the mechanisms involved.

There are two primary sources of outgassing species:

- Low molecular weight (LMW) siloxanes that are present in the uncured silicone.
- LMW siloxanes that are the products of the degradation of the material at elevated temperatures.

Both of these sources are difficult to avoid for most silicone manufacturers. LMW siloxanes are present in silicone formulations because they are needed to facilitate the processing and mixing of pigments and other essential components. Degradation of the polymer, which is constantly producing LMW siloxanes, proceeds at a very slow rate at lower temperatures but has an appreciable rate at higher temperatures, which are typical of many applications.¹ While it may not be possible to eliminate all outgassing species, by understanding the mechanisms involved, some silicone manufacturers have been successful in reducing outgassing by almost an order of magnitude.

Outgassing occurs in two fundamental steps. First, LMW siloxanes diffuse to the surface of the elastomer. Second, at the surface of the elastomer, desorption of the siloxanes occurs as they are released into the surrounding environment. In conditions where the concentration of LMW siloxanes in the air near the surface of the elastomer is low or negligible, desorption occurs quickly and is not a rate-limiting step. This is the case in applications where the silicone is not encapsulated and there is sufficient airflow.



Here is an example of an LMW cyclic siloxane that will outgas. Cyclics are formed during depolymerization or reversion reactions.

The diffusion step is more important in determining the rate of outgassing. A great deal of research into this subject has been driven by power cable designers who use silicone insulation and are interested in understanding the unique ability of silicone to recover its hydrophobicity after exposure to corona discharges and pollution. This recovery is accomplished by the diffusion of low molecular weight siloxanes toward the surface of the insulation, which acts to hydrophobically seal the surface.

In these studies, diffusion of LMW siloxane in silicones has been modeled as a function of the square root of time.² Empirical studies tend to confirm this model.

Understanding the sources and mechanisms of outgassing has led to the development of low outgassing silicones by allowing researchers to attack both the sources of outgassing as well as optimizing processes used to diffuse out LMW siloxanes cost effectively. Newer formulations using unique chemistries and processing methods have reduced outgassing by nearly one-third. Figure 1 shows an example of two materials and the results obtained from developmental work in this area. Outgassing normally is measured by the total mass lost (%TML) at a specific temperature, pressure and over a given period of time. (Typically, 250°F [121°C], 10-5 atm, and 24

hr, respectively, are used.) As illustrated, outgassing can range from 4.5 percent mass lost with traditional silicones to less than 1 percent with newer technologies.

For decades, silicone and silicone composites have been a major insulation platform for high temperature flexible heaters. While silicone offers numerous performance advantages, outgassing concerns have limited its use for some applications. Significant research has been done to identify the sources and mechanisms of silicone outgassing, which has resulted in ways to significantly reduce the content of low molecular weight siloxane species and processing methods to reduce the evolution of outgassing while in service. These advances now allow for broader use of silicone in sensitive applications where outgassing concerns have previously limited its use.

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